

## REPORT DOCUMENTATION PAGE

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| <b>14. ABSTRACT</b><br>Improved multiscale molecular dynamics simulation methods will permit application of computational chemical methods to large molecules including propellants. Higher performance propellants are needed for Air Force rocket propulsion applications to put heavier payloads into space at lower cost. Rocket fuels with substantially increased performance over conventional propellants would be an enabling technology for such missions as single-stage-to-orbit applications. This work helps develop a full spectrum of theoretical tools to predict, characterize, and contribute to synthesizing novel high energy density materials. |                                    |   |   |  |   |
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**FINAL PERFORMANCE REPORT**  
**7/1/07 – 6/30/08**

**Submitted to**  
**The Air Force Office of Scientific Research**  
**DURIP FA9550-07-1-0526**

**Instrumentation for Atomic Layer Deposition and Single Molecule  
SERS/TERS Excitation Spectroscopy**

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## 2. Goal of Equipment Purchase

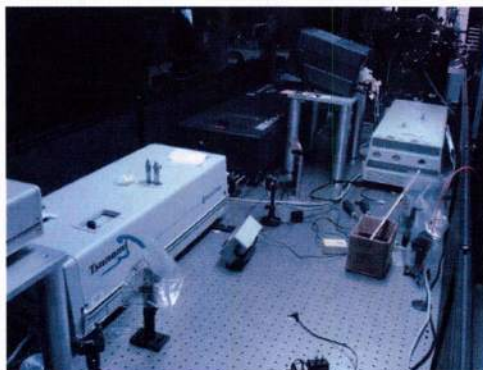
The primary goal of DURIP FA9550-07-1-0526 was to add the following capabilities to the research effort focused on the design, development, and implementation of new ultrasensitive, multidimensional, surface-enhanced spectroscopies: (1) augment existing laser system to provide continuous, gap-free wavelength tuning from 233 nm to 3300 nm and (2) implement *in-situ* surface-enhanced Raman spectroscopy in an existing atomic layer deposition reactor.

## 3. Summary of Equipment Purchased

### A. Visible, Ultrafast Optical Parametric Oscillator

A Coherent Mira-OPO (Figure 1) was purchased to extend the tuning range of our existing laser system to include wavelengths of 505nm-750nm and 1000nm-3300nm. In combination with the existing lasers, the complete system can generate wavelengths from 233-3300nm continuously, allowing study of the surface-enhanced Raman excitation profiles in any spectral region. This new, fully automated optical parametric oscillator has the following features:

- Periodically-poled KTP and temperature-controlled BBO crystals for broad phase-matching, allowing for automated wavelength tuning without need for realignment.
- External wavelength meter for monitoring spectral position and bandwidth.
- Cavity stabilization via a nanopositioning motor for low wavelength drift.
- Signal and idler output from 1000nm-1600nm and 1600nm-3300nm, respectively. Intracavity second harmonic generation of the signal beam provides 500nm-750nm wavelengths. Access to signal, idler, second harmonic and depleted pump available simultaneously, allowing for potential non-linear and time-resolved studies.
- Capable of operating from both pico- and femtosecond pump pulses. Picosecond pulses are attractive for Raman spectroscopy due to the narrower bandwidth, negating the need for external bandwidth filtering.

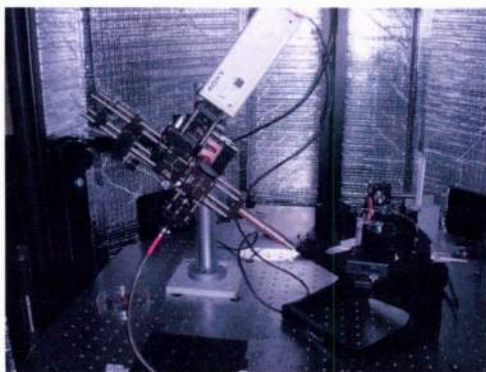


**Figure 1.** The Coherent Mira-OPO optical parametric oscillator with existing laser system. Other components include a Spectra-Physics Tsunami Ti:Sapphire oscillator and a Spectra-Physics GWU second and third harmonic generator.

### B. Lasers for Tip-Enhanced Raman Spectroscopy (TERS)

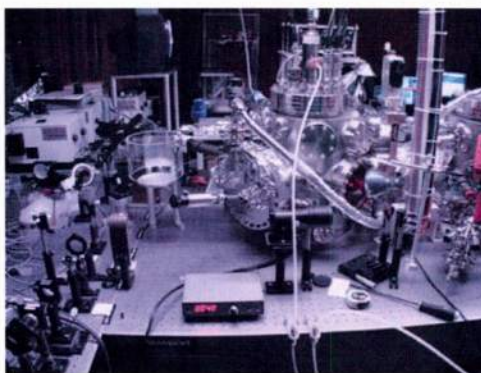
Two lasers were purchased to support the research effort in tip-enhanced Raman spectroscopy. The first is a Coherent Cube 640nm with fiber pigtail (Figure 2), which is integrated with an ambient scanning tunneling microscope (Agilent scanner, RHK control

electronics). The laser is capable of producing 20mW of 640nm light at the output of a single-mode, polarization-maintaining fiber optic. This tip-enhanced Raman instrument was built to rapidly evaluate tip preparation procedures and study single molecule tip-enhanced Raman under ambient conditions.



**Figure 2.** The Coherent Cube laser integrated with the scanning tunneling microscope via a homebuilt optical microscope.

The second laser for tip-enhanced Raman is a Spectra-Physics 632.8nm HeNe (Figure 3) with 12mW of polarized power. This laser is interfaced with a homebuilt, cryogenic, scanning tunneling microscope in an ultra-high vacuum chamber. The primary purpose of the laser is to test atomic resolution imaging while the plasmonic tip is being irradiated.



**Figure 3.** The Spectra-Physics HeNe laser interfaced with the ultra-high vacuum, cryogenic scanning tunneling microscope.

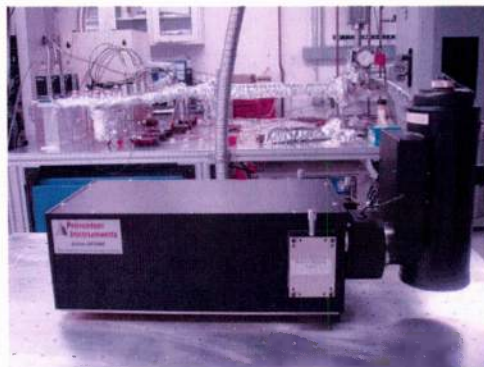
### C. *in-Situ* Surface-Enhanced Raman Spectroscopy Capability to Atomic Layer Deposition Reactor

An Acton 2500i 1/2-meter spectrograph and Princeton Instruments Spec-10:100B CCD detector (Figure 4) have been purchased for integration with an existing atomic layer deposition reactor. This system will add the capability of *in-situ* surface-enhanced Raman spectroscopy and



localized surface Plasmon resonance extinction spectroscopy during the atomic layer deposition process. Features of this detection system include:

- Back-thinned CCD detector for high quantum efficiency (>90%).
- Liquid nitrogen cooling for low dark current, allowing long acquisition times.
- Low noise analog-to-digital (<3 e-) for optimum signal-to-noise.
- Three gratings allowing flexibility with respect to spectral range and resolution.
- Availability of fiber-optic coupling hardware.
- Exit slit for single channel detection for time-resolved studies.

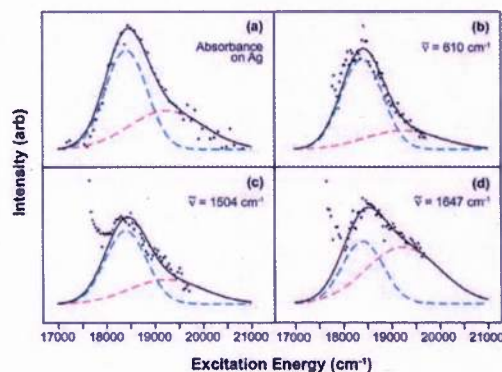


**Figure 4.** The Raman detection system with the atomic layer deposition reactor.

#### 4. Accomplishments/New Findings

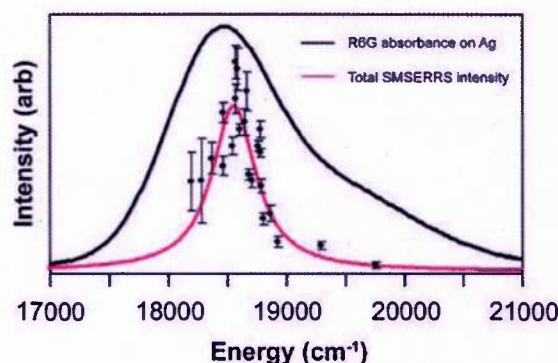
##### A. Visible, Ultrafast Optical Parametric Oscillator

The Coherent Mira-OPO has been actively involved in the study of surface-enhanced Raman excitation profiles (REPs) of rhodamine 6G (R6G) on Ag surfaces. The optical parametric oscillator affords the ability to finely tune the excitation wavelength near the molecular resonance of R6G (i.e.,  $\lambda=500\text{ nm}-575\text{ nm}$ ) and perform wavelength-scanned surface-enhanced Raman excitation measurements of a single molecule. The ensemble-averaged surface-enhanced REPs were measured for collections of molecules on Ag island films. The relative contributions of the 0-0 and 0-1 vibronic transitions to the surface-enhanced REPs vary with vibrational frequency. (Figure 5) These results highlight the role of excitation energy in



**Figure 5.** Absorbance of R6G on Ag (a). Ensemble-averaged surface-enhanced Raman excitation profiles of different Raman modes of R6G on AgIF. (b)  $\nu = 610$ , (c)  $1504$ , and (d)  $1647\text{ cm}^{-1}$  ( $P_{\text{ex}} \approx 150\text{ W}\cdot\text{cm}^{-2}$ ,  $t_{\text{ac}} = 20\text{ s}$ ). The black solid lines represent a fit of the data (points) to a sum of two Gaussians. The dashed lines correspond to the deconvolution of the overall fit, demonstrating relative contributions from the 0-0 and 0-1 vibronic transitions of R6G on Ag ( $E_{\text{max}} = 18409\text{ cm}^{-1}$ ,  $\text{fwhm} = 1004\text{ cm}^{-1}$  and  $E_{\text{max}} = 19246\text{ cm}^{-1}$ ,  $\text{fwhm} = 1822\text{ cm}^{-1}$ ).

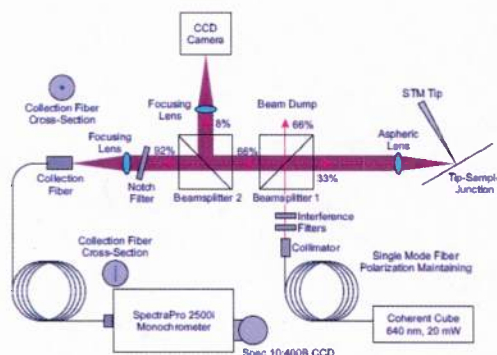
determining the resonance Raman intensities for R6G on surface-enhancing nanostructures. Single-molecule measurements were obtained from individual molecules of R6G on Ag colloidal aggregates, where single-molecule junctions are located using the isotope-edited approach. Overall, single-molecule surface-enhanced REPs are narrow in comparison to the ensemble-averaged excitation profiles due to a reduction in inhomogeneous broadening. (Figure 6) These results describe the first Raman excitation spectroscopy studies of a single molecule, revealing new information previously obscured by the ensemble.



**Figure 6.** Comparison of the single-molecule surface-enhanced resonance REP of R6G to the ensemble-averaged surface absorbance spectrum on Ag. The single-molecule REP (points) was obtained from the sum of all observed Raman modes and was fit to a Lorentzian function (red solid line) where the error represents one standard deviation from the mean ( $E_{\text{max}} = 18563 \text{ cm}^{-1}$  and  $\text{fwhm} = 449 \text{ cm}^{-1}$ ). The molecular absorbance of R6G on 200 nm Ag film (black) was fit by a sum of two Gaussians. As expected, the single-molecule data are significantly narrower than the ensemble-averaged analogue ( $\sim 1100 \text{ cm}^{-1}$ ).

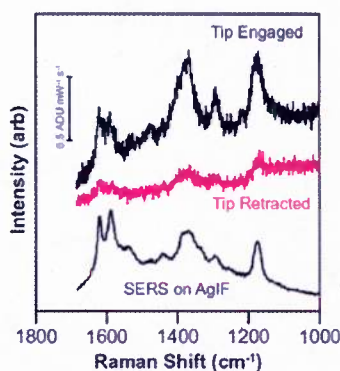
## B. Ambient Tip-Enhanced Raman Spectroscopy (TERS)

The Coherent 640 nm cube laser was interfaced with a homebuilt Raman microscope for tip-enhanced Raman studies. The optical Raman microscope consists of three major components: 1) the Coherent Cube direct diode laser excitation source launched into a single-mode, polarization-maintaining optical fiber, 2) a home built optical microscope and 3) a fiber-coupled detection system with single-stage spectrometer and CCD detector. (Figure 7)



**Figure 7.** Instrument diagram for ambient tip-enhanced Raman spectroscopy.

A chemically-etched Ag tip and Ag substrate (200 nm Ag on ITO) with monolayer crystal violet were mounted in the instrument. First, a surface-enhanced Raman spectrum from the Ag surface was collected to determine the background surface-enhanced signal (excitation power = 0.60 mW, acquisition time = 20 s). The surface-enhanced Raman spectrum shows weak signal corresponding to the modes of crystal violet. Then, the Ag tip was brought into tunneling range. The tip-enhanced Raman spectrum shows a large increase in signal corresponding to crystal violet over the surface-enhanced background. (Figure 8) One issue often found in tip-enhanced Raman spectroscopy is contrast, whereas the signal generated by the surface dominates and the additional tip-enhanced signal afforded at the tip-sample junction is lost in the background. Because only 50-100 molecules are excited in the tip-sample junction, it is estimated that the tip-derived enhancement factor is of order  $10^5$ - $10^6$ . Currently, experiments are being performed to push tip-enhanced Raman spectroscopy to the ultimate limit of detection, a



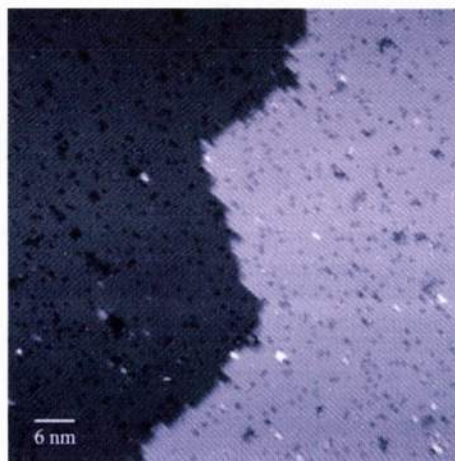
**Figure 8.** Tip-enhanced Raman spectrum of crystal violet adsorbed to Ag surface with electrochemically etched Ag tip. Tip engaged (black line) and tip retracted (red line). Excitation power = 0.60 mW, acquisition time = 20 s. For comparison, a surface-enhanced Raman spectrum of crystal violet on Ag island film is shown. Excitation power = 3.0 mW, acquisition time = 5 s.

single molecule.

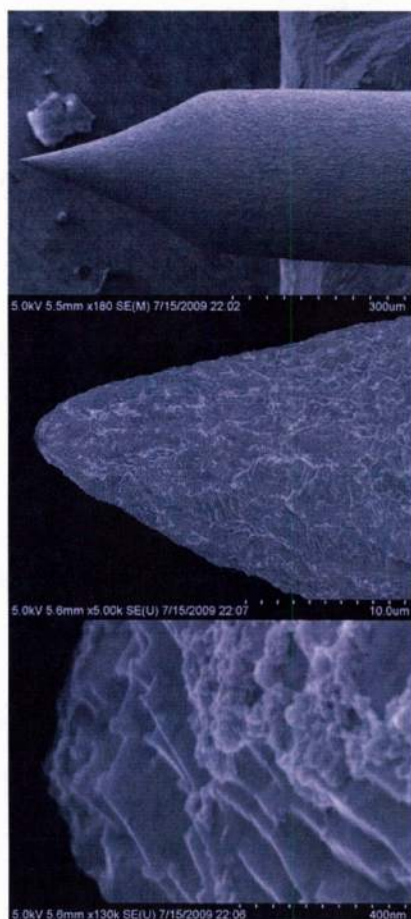
### C. Atomic Resolution Imaging with an Irradiated Plasmonic Tip

Experiments are being performed to test the ability of the scanning tunneling microscope to maintain a stable tunneling current under various laser conditions and achieve atomic resolution imaging. A Spectra-Physics 632.8 nm HeNe laser was focused onto the tip-sample junction. Although the tip undergoes laser-induced heating, results indicate that the system equilibrates rapidly and stabilizes after a few minutes. Upon equilibration, atomic resolution imaging is achievable at room temperature with a Ag plasmonic tip under similar power and excitation wavelength conditions as the ambient tip-enhanced results shown. (Figure 9) These images show clear resolution of Si(100) dimer rows, step edges, defects, and molecular adsorbates. An SEM image of the probe (Figure 10) reveals a tip radius of curvature of ca. 20 nm. This represents the first atomic scale spatial resolution with a plasmonic tip, important for correlated high resolution imaging and highly sensitive Raman detection. For these studies, detection will be performed with a subtractive triple spectrograph for tunable excitation laser rejection and inelastically scattered light is collected with a deep-depletion CCD detector. Additionally, this system is interfaced with the broadly tunable laser system for study of tip-enhanced Raman excitation profiles. This will provide insight into the plasmonic nature of the Ag tip, which is difficult to measure directly.





**Figure 9.** Scanning tunneling microscope image of Si(100) with the Raman laser on. Excitation by Spectra-Physics 632.8 nm HeNe laser at 0.60 mW.



**Figure 10.** Scanning electron microscopy image of the electrochemically prepared Ag tip for atomic resolution imaging. The tip radius of curvature is approximately 20 nm.